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Dynamic response of the spin-crossover solid $Co(H_2(fsa)_2en)(py)_2$ to a pulsed magnetic field

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The spin transition between the paramagnetic high-spin (HS) and low-spin (LS) electronic states of $Co^{II}(H_2(fsa)_2en)(py)_2$, $[H_2(fsa)_2en$=N,N′-ethylene bis(3-carboxysalicylaldimine), py=pyridine$]$ under a pulsed and intense magnetic field (32 T) has been probed by optical reflectivity. In the absence of perturbation, a thermal hysteresis loop ($\Delta T = 19.4$ K, $T_{1/2} = 126$ K) was detected. Applying a magnetic field of 32 T to the solid, the initial state of which belongs to the ascending branch of the hysteresis loop, leads to an irreversible and quasicomplete $S=1/2 \rightarrow S=3/2$ transition. The experimental evidence of this crossover triggered by a pulsed magnetic field is reported here in conjunction with an adequate Ising-like model. This two-level model, used as a first approach, allows us to reproduce quantitatively the -4.9 K shift in transition temperature under the effect of the 32 T static magnetic field. The dynamic aspects of the previous model are also explored, leading to a description of the main features of the phenomenon. Indeed, an irreversible (reversible) jump of the high-spin fraction is predicted when the pulsed magnetic field is applied in the metastable LS (HS) phase.

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Spin-crossover (SC) materials, studied extensively for their thermo-, piezo-, photo-, and magnetochromic properties,[1] seem to have promising potentialities as high-density reinscribable memories. Indeed, the state of such bistable systems can be addressed on the molecular scale. The variety of properties displayed by such systems might be employed in writing or reading processes. From this point of view, a synergy between the elaboration of new materials and the study of mechanisms which govern addressing of information should be tentatively sought. In this respect, the understanding and control of the dynamic processes between the macroscopic metastable and stable states appears to be crucial. This field has a strong connection with the very active and more general theme of the dynamics of phase transitions[2] and justifies the intense collaboration between the scientific communities of chemists and physicists.

The discovery of the light-induced excited spin-state trapping (LIESST) effect[3] in spin-crossover systems has opened a new field of investigation, i.e., the study of out-of-equilibrium properties in such systems. Photoinduced bistability studied from the experimental[4] and theoretical[5] points of view affords typical examples. Recently, Ogawa *et al.*[6] have reported that the LIESST effect can show nonlinear characteristics such as thresholdlike behavior, incubation time, and phase separation, suggesting the existence of a cooperative photoinduced phase transition in SC solids. Recently, partial triggering of the iron(II) spin crossover in solid $Fe(Phen)_2NCS_2$ has also been evidenced upon application of a high magnetic field in the hysteresis loop.[7]

We report here the possibility of a quasicomplete commutation of cobalt(II) between the two states of a SC system by a pulsed magnetic field (PMF). Choosing a cobalt-based SC system follows the idea that cobalt(II) materials as well as iron(III) ones have metal-ligand bonds shorter than those in iron(II) materials, leading to faster relaxation dynamics between the high-spin (HS) and low-spin (LS) states, which should enhance the PMF addressing of SC. We also report on a theoretical analysis based on a stochastic approach of the dynamic behavior of the high-spin fraction under applied PMF.

For this study, we have thus prepared the SC complex $Co^{II}(H_2(fsa)_2en)(py)_2$ $[H_2(fsa)en$=N,N′-ethylene bis(3-carboxysalicylaldimine,py)=pyridine$]$ following the method described by Torihara *et al.*[8] If the energy barriers in the solid state are thermally accessible, cobalt(II) (d^7) in the previous molecule may be either in the LS state ($t_{2g}^6 e_{2g}^1, S=1/2$) or in the HS state ($t_{2g}^5 e_{2g}^2, S=3/2$), both of which are paramagnetic and correspond to strong and weak ligand field energies, respectively. At the macroscopic level, an external perturbation such as temperature, pressure, light, or magnetic field can induce a spin crossover between the two states. The spin transition in $Co(H_2(fsa)_2en)(py)_2$ is also associated with a color change and can thus be probed by reflectivity measurements. Indeed, the color of the sample changes from red in the LS state to orange in the HS state.

Figure 1 shows the temperature dependence of the HS fraction of the sample, which consists in an abrupt thermally induced spin crossover. This first-order transition, evidenced by a 19-K-wide hysteresis loop centered at 126 K, is observed by reflectivity measurements[9] on a microcrystalline sample (15 mg) of $Co(H_2(fsa)_2en)py2$.

To carry out the experiments of magnetoswitching in molecular spin-crossover systems, we have used the experimental facility of the Laboratoire National des Champs Magnetiques Pulsés (LNCMP) which produces high magnetic fields [up to 32 T (Fig. 2) and very recently 60 T] of long duration, by discharge in the resistive coil of a battery of condensers (1.25 MJ, 25000 μF) beforehand charged under a 0–10 kV voltage.

The cobalt(II) HS fraction, denoted n_{HS}, can be probed instantaneously with an optical reflectivity setup[9] utilizing a continuous helium-neon laser (632.8 nm) irradiation with a power of 5 mW.

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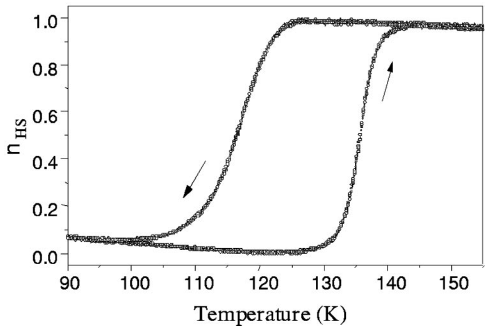

FIG. 1. Thermal hysteresis [high-spin fraction (n_{HS}) vs temperature] of $\mathrm{Co(H_2(fsa)_2en)(py_2)}$, obtained by reflectivity measurements.

The PMF shown in Fig. 2 has been applied to various states of the metastable HS and LS phases, corresponding to initial states of equilibrium in the descending and ascending branches of the thermal hysteresis loop shown in Fig. 1, respectively. The results obtained are displayed with the n_{HS} curves (B) in Figs. 3 and 4. Figure 3 shows that application of the high magnetic field is without any effect on the descending branch of the hysteresis loop. Indeed, in this case, the initial state is a metastable HS one, and the effect of the PMF is to increase the free-energy barrier, further stabilizing the HS phase. Therefore, the PMF effect naturally leads to a reversible evolution of the HS fraction.

When the high magnetic field is applied in the ascending branch of the thermal cycle, corresponding to the metastable LS phase (Fig. 4), the latter is destabilized and the HS fraction grows irreversibly according to the nucleation and growth process, which continues beyond the duration of the perturbation. In this region, all metastable LS domains, initially close to an unstable state, switch owing to the magnetic field. Quantitatively, Fig. 4 shows that for an initial n_{HS} fraction ~0.3, the magnetic field induces a quasitotal irreversible triggering of the spin transition with an increase of approximately 60% of the HS fraction. On the time scale of the observation, no delay between the magnetic excitation $B(t)$ and the response $n_{\mathrm{HS}}(t)$ of the system is observed. In addition, the final HS state (denoted n_{HS}^f) induced by the field is very long lived.

It is also remarkable that the amplitude $\Delta n_{\mathrm{HS}} = n_{\mathrm{HS}}^f - n_{\mathrm{HS}}^0$ of the spin state change strongly depends on the initial state n_{HS}^0 (Fig. 5). Indeed, the experimental data represented by triangles show that Δn_{HS} is maximum when $n_{\mathrm{HS}}^0 \approx 0.2$; Δn_{HS} decreases quite sharply when the PMF is applied on both sides of this value.

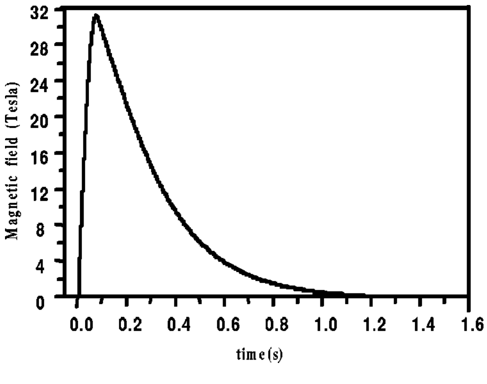

FIG. 2. Time dependence of the applied magnetic field pulse.

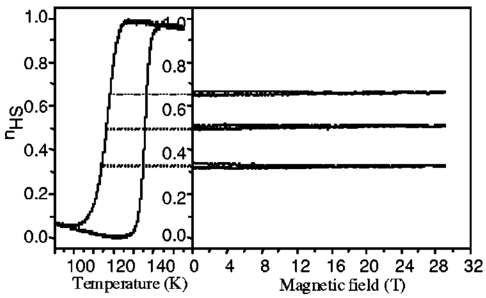

FIG. 3. The reversible response of a HS fraction in $\mathrm{Co(H_2(fsa)_2en)(py)_2}$ to an applied PMF in the metastable HS state.

On the other hand, this maximum efficiency in PMF addressing has to be correlated with the thermal evolution of the magnetic susceptibility of the system which also presents a maximum in this temperature range. Such a relation may be obtained using simple considerations in the adiabatic approach.

First, it is straightforward to consider that the magnetic field, which stabilizes more the HS than the LS state, induces a shift ΔT_c of the transition temperature. In a macroscopic quasistatic approach, this transition temperature shift is given by $\Delta T_c = -\Delta\chi B^2/2\Delta S$,[7] where $\Delta\chi$ is the change in magnetic susceptibility and ΔS is the entropy variation. Using the experimentally obtained values for $\Delta\chi$ and ΔS,[10] we find that when the magnetic field is increased up to 32 T, both transition temperatures of the thermal hysteresis loop decrease by 4.9 K, which is quite important. This result allows us to determine, in the frame of this adiabatic approximation, the amplitudes Δn_{HS} of the changes. The results obtained are plotted as squares in Fig. 5, and they are in quite good agreement with the experimental data. In particular, this first simple approach allows a quite good localization of the n_{HS} region where the response of the system to the magnetic field effect is enhanced.

From the microscopic theoretical point of view, a cooperative spin-crossover solid under a magnetic field $\mathbf{B}$ can be described by an extended Ising-like model,[11] for which the Hamiltonian is written as

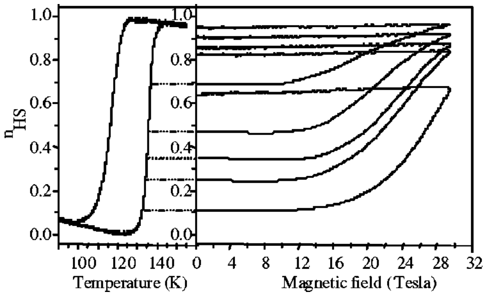

FIG. 4. Set of isotherms $n_{\mathrm{HS}}(B)$ showing the irreversible (and quasitotal) triggering effect on the HS fraction in $\mathrm{Co(H_2(fsa)_2en)(py)_2}$ for an applied PMF in the metastable LS state.

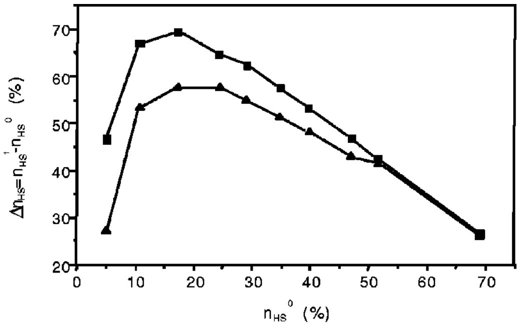

FIG. 5. Comparison of the amplitudes of conversion in Co(H$_2$(fsa)$_2$en)py$_2$ obtained experimentally (triangles) and by using the quasistatic approach (squares).

$$\hat{\mathbf{H}}=\frac{\Delta_0-kT\ln g_+/g_-}{2}\sum_i \hat{\sigma}_i-\sum_{i\neq j} J\hat{\sigma}_i\hat{\sigma}_j -g_L\mu B\hat{S}_z^H\sum_i \frac{\hat{\sigma}_i+1}{2}-g_L\mu\hat{S}_z^L B\sum_i \frac{1-\hat{\sigma}_i}{2}. \qquad (1)$$

In this specific Hamiltonian, the HS and LS states are associated, respectively, with the eigenvalues $+1$ and -1 of the fictitious spin operator σ with their respective different degeneracies g_+ and g_-. Here $2\Delta_0$ is the energy difference $E(\mathrm{HS})-E(\mathrm{LS})$ for isolated molecules, and J accounts for ferroelastic interactions between neighboring molecules. The last two terms are the Zeeman contribution in the HS and LS states, respectively, where μ is the Bohr magneton, g_L the Landé factor, and $S_{H,L}$ is the magnetic spin moment corresponding to the HS and LS states. In absence of a magnetic field, the transition temperature $T_{1/2}$, obtained for equal populations of HS and LS states, is given by $T_{1/2}=\Delta_0/k_B\ln(g_+/g_-)$. Under a static magnetic field B, such as $g_L\mu B\ll kT_{1/2}$, the shift of the transition temperature $\delta T_{1/2}$ is expected to be given by

$$\delta T_{1/2}=-\frac{g_L^2\mu^2B^2}{24k_B\Delta_0}[(2S_H+1)^2-(2S_L+1)^2].$$

In the case of Co(H$_2$(fsa)en)py$_2$ for which $S_H=3/2$, $S_L=1/2$, $\Delta_0=700$ K,[10] under a magnetic field of 32 T we obtain $\delta T_{1/2}=-2(\mu_B B)^2/k_B\Delta_0\approx-4.9$ K. This negative shift in temperature clearly indicates that the application of the magnetic field stabilizes (destabilizes) the HS (LS) phase.

The dynamic version of this model requires a stochastic description[12] based on the following master equations:

$$\frac{d}{dt}p(\{\sigma\},t)=\sum_j W_j(-\sigma_j)p(\{\sigma_j\}-\sigma_j;t) -\sum_j W_j(\sigma_j)p(\{\sigma_j\}\sigma_j;t) \qquad (2)$$

$p(\{\sigma\},t)$ is the probability for observing the system in the configuration $\{\sigma\}=(\sigma_1,\sigma_2,\dots,\sigma_N)$ at time t, and $\{\sigma\}_j$ denotes the configuration of all spins except σ_j. Here $W_j(\sigma_j)$ are the transition rates of the spin flip $\sigma_j\rightarrow-\sigma_j$, induced by the thermal bath which are constrained to respect the microscopic detailed balance condition.

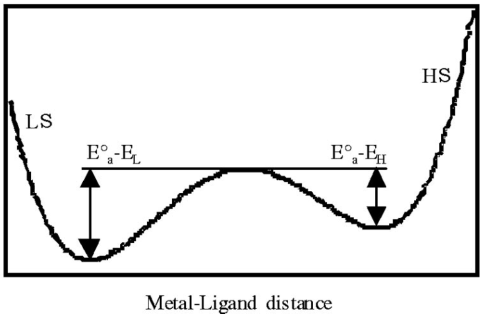

FIG. 6. Vibronic intramolecular energy barrier E_a^0 for a SC system. E_H and E_L are the energies of the HS and LS states, respectively.

Due to the existence of a vibronic energy barrier between the HS and LS states at the molecular level, as shown in Fig. 6, the convenient dynamics for the SC problem at high temperature is based on an Arrhenius-like process.[13] Let us denote by E_a^0 the energy barrier between the HS and LS states when they have the same energy, by E_H and E_L their respective energies, and by $W(H\leftrightarrow L)$ the transition rates between the two states. Therefore, $W(H\rightarrow L)\propto e^{-\beta(E_a^0-E_H)}$, and consequently the general form of the rate transition can be written as $W_j(\sigma_j)=(1/2\tau_0)e^{-\beta(E_a^0+\sigma_jE_j)}$ in which $1/\tau_0$ defines the individual spin-flip rate between the two states and

$$E_j=-\frac{\Delta_0}{2}+2\frac{(\mu B)^2}{kT}+\frac{kT}{2}\ln\frac{g_+}{g_-}+J\sum_i \sigma_i.$$

Inserting this form of transition rates into the master equation (2), we may calculate the temporal evolution of the "magnetization" $m=\langle\sigma_j\rangle$. In the mean-field approximation,[13] we obtain the following nonlinear differential equation for the HS fraction of molecules, $n_{\mathrm{HS}}=(1+m)/2$:

$$\frac{dn_{\mathrm{HS}}}{dt}=-\frac{2}{\tau_0}n_{\mathrm{HS}}e^{-\beta\varepsilon^+}e^{-2\beta qJn_{\mathrm{HS}}} +\frac{2}{\tau_0}(1-n_{\mathrm{HS}})e^{-\beta\varepsilon^-}e^{2\beta qJn_{\mathrm{HS}}}, \qquad (3)$$

with

$$\varepsilon^{\pm}=\pm E_a^0\mp\frac{\Delta_0}{2}\mp qJ\pm\frac{kT}{2}\ln 2\frac{g_{\mathrm{HS}}}{g_{\mathrm{LS}}}\pm 2\frac{[\mu B(t)]^2}{kT}.$$

To qualitatively compare the present model with the experimental results, we have resolved Eq. (3) in the ascending and descending branches of the thermal hysteresis loop, for the magnetic pulse represented in Fig. 2. The results obtained in the heating mode, summarized in Fig. 7, lead to the following conclusion: (i) this model is qualitatively in good agreement with the experimental behavior, and (ii) it clearly shows that the nonreversible variation of the high-spin fraction is well reproduced, and the amplitude δn_{HS} of the irreversibility depends on the initial state, as found in the experi-

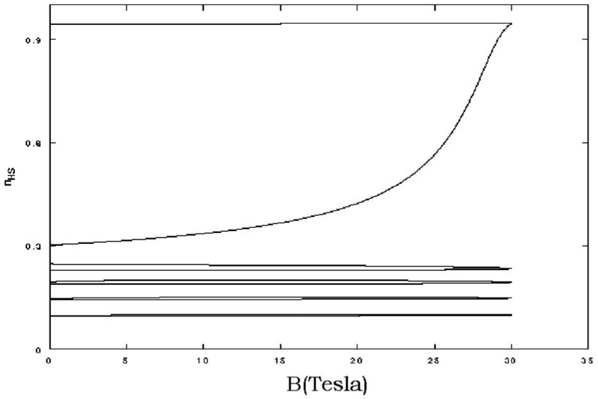

FIG. 7. Calculated HS fraction as a function of the pulsed magnetic field **B** in the ascending branch of the hysteresis loop.

ments. In the same way, the reversible character of the evolution of the HS fraction under a pulsed magnetic field is also found when the latter is applied in the descending branch of the hysteresis loop.

In addition, this approach shows that the efficiency of the LS→HS addressing depends on various parameters, including the frequency $1/\tau_0$ of individual spin flip, the strength of the vibronic coupling (from which the energy barrier E_0^a originates), and the transition temperature $T_{1/2}$. Indeed, the same magnetic pulse applied to $Fe(Phen)_2(NCS)_2$ (Ref. 7) produces a jump in HS fraction 60% weaker than that obtained with $Co(H_2(fsa)_2en)(py)_2$. These results are in very good agreement with the respective shifts in transition temperature, $\delta T_{1/2} = -1.9$ K and -4.9 K. Moreover, it is well known from the literature[14] that relaxation is slower in iron(II) compared to cobalt or iron(III) spin-crossover complexes, due to differences in the strength of the vibronic coupling.

It is also worth mentioning that the nonreversibility of the response is enhanced when the transition temperature is low, and this is definitely in favor of $Co(H_2(fsa)2en)(py)_2$ for which $T_{1/2} = 130$ K [$T_{1/2} = 180$ K for $Fe(Phen)_2(NCS)_2$ (Ref. 5)]. It is also interesting to remark that, as an immediate consequence of the fast dynamics, the nonlinear effects of the interactions are hidden in $Co(H_2(fsa)en)py_2$, while they are visible in $Fe(Phen)_2(NCS)_2$ owing to the appearance of a temporal delay between the excitation (magnetic pulse) and the response (increase in HS fraction).

In conclusion, we have reported here on a quasitotal triggering of spin crossover by a high magnetic field pulse (32 T). This efficiency of the PMF is based on the main idea that the strength of the vibronic coupling governs the relaxation rate (transition rate). This factor appears crucial in realizing an effective control of the LS→HS transition for addressing information with a magnetic field; the addressed information can be read optically. From the theoretical point of view, the static and dynamic effects observed are well reproduced by an extended Ising-like model including the magnetic field effect: they correspond, respectively, to a shift of the transition temperature and a specific nonlinear time-dependent behavior of the HS fraction under a pulsed magnetic field.

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